Development of an Inking System for Continuous Roll-to-Roll Microcontact Printing of Hexadecanethiol (HDT) on Gold-coated PET Substrate

by

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B.S. Mechanical Engineering, University of California, Berkeley (2014)

Submitted to the Department of Mechanical Engineering in partial fulfillment of the requirements for the degree of Master of Science in Mechanical Engineering at the MASSACHUSETTS INSTITUTE OF TECHNOLOGY

June 2016

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Abstract

Microcontact printing is a form of soft lithography that employs a molded polymer stamp to print substrates with pattern features as small as the sub-micron range. This is traditionally a plate-to-plate printing process, employing both flat stamps and flat, rigid substrates. However, to utilize this patterning technique in a truly low cost manner, it must evolve to a scalable roll-to-roll process. This combination of high precision patterning with high throughput manufacturing techniques could both reduce cost of current products, as well as enable a range of new technologies. Large area, high rate, continuous microcontact printing could be used to make flexible displays, photovoltaic dust sensors, and large area sensors among other products.

This work describes the development of an inking system to enable continuous, roll-to-roll microcontact printing on a lab-scale machine. The molecular ink hexadecanethiol (HDT) is used to print self-assembling monolayers (SAMs) on flexible, gold-coated PET substrate. An ink tank and dryer system are designed and built to enable this material combination to be printed in a continuous manner. Measurement of print quality and pattern replication is executed to confirm that the system performs suitably at high throughput. The employment of the inking system facilitates a continuous, roll-to-roll microcontact printing process which can be used to further develop this manufacturing strategy.

Thesis Supervisor: David E. Hardt
Title: Ralph E. Cross and Eloise F. Cross Professor of Mechanical Engineering
Acknowledgments

My studies at MIT, as well as those before, would not have been possible without the support of my family, especially my loving parents. They laid the groundwork for me to be here, and it means so much to me to be able to follow my dreams. I am truly grateful for how much they have helped me along the way.

I would like to thank my advisor, Dave Hardt, for his much-needed guidance in my time here. His advice and support, both academic and otherwise, helped me keep an even keel and navigate the churning waters of my studies. I always enjoyed the time I shared with him and am glad I learned so much.

My friends here, especially those in the department, were instrumental in my success. Whether we were doing problem sets, building our latest project, or just having fun, my peers were there for me. The community was always supportive and helpful, and I am ever grateful. I can only hope the relationships I have built here will continue to grow stronger.

I must also thank my funding sources who have made this possible, especially the Wheless Fellowship. This project was funded and supported by the Center for Clean Water and Clean Energy, a collaboration between between MIT and King Fahd University of Petroleum and Minerals (KFUPM). The support, especially from Hussain AlQahtani and Muhammad Hawwa, was greatly appreciated.
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Chapter 1

Introduction

1.1 Overview of Microcontact Printing

Microcontact printing is a form of soft lithography developed by Xia and Whitesides to create sub-micron scale patterns of surface deposits using compliant printing stamps [1]. The process involves the transfer of self-assembling molecular monolayers from patterned elastomer stamps [2],[3] and has emerged in the last decade as a leading candidate for full-scale commercial production of nano-patterned surfaces [4]. These stamps are typically cast from the elastomer polydimethylsiloxane (PDMS) and feature replication down to <80 nm has been demonstrated [5]. It differs from traditional printing not only because of the sub-micron features size, but also because of the basic physics of the ink transfer. The typical inks used are a class of self-assembling molecules, typically alkanethiols, that are applied to the stamp and transferred dry to the substrate. Once transferred these molecules self-assemble into a monolayer on the surface, which changes the surface properties in significant ways. Depending on the substrate used, these changes can lead to significant variation in surface energy [6], serve as a chemical etch resist [7], or, if combined with appropriate catalysts, provide a template for metal, silicon or carbon nanotube (CNT) growth [8]. In all these applications, the key manufacturing challenge is to consistently create the basic surface pattern on a large area, high-rate basis.

Roll-to-roll printing is an established technique of printing used to pattern flexible
substrates such as paper and plastic films. The substrate, known as the ‘web’, is thin and flexible, so it can be transported over rollers for printing or other processes. Modern newspaper presses print tens of thousands of copies per hour with this method, which is an incredible feat of throughput. Combining microcontact printing with this roll-to-roll technique makes sense to scale the throughput beyond the lab scale. Roll-to-roll microcontact printing to achieve large-scale, continuous production is the challenge addressed by this research.

1.2 Potential Applications

The core development of large area, high rate microcontact printing is helpful because of the cost reduction afforded to patterning small features onto large areas of flexible substrate. This can be applied either to reduce cost of existing technologies or to enable new technologies. Flexible electronics, for example, is a growing business area with consumer products already available, though it is currently dominated by other patterning strategies, such as inkjet printing [9]. Large area sensors, especially with regard to photovoltaics, could benefit from capabilities to pattern significantly larger areas than modern lithographic wafer sizes. Lastly, lithium ion battery electrodes, which are currently difficult to manufacture, could be printed with CNTs to improve both manufacturability and efficiency.

1.2.1 Flexible Electronics

The consumer electronics industry is enormous: just the flexible AMOLED display market was worth around $4 billion in 2015, and it is predicted to grow into the tens of billions in the coming years [10]. The flexible consumer electronics currently available are rather limited, however. The modern smartphone is still a rigid device, but flexible electronic technology has crept in in a variety of locations, most notably the displays. The Galaxy S7 Edge is one of the first phones to have a display created on a flexible substrate [10]. Non-contact deposition methods, such as slot die coating and inkjet printing, currently dominate these areas.

Roll-to-roll processing is cost effective at large throughput because it is a parallel
process. Instead of processing one display at a time, multiple displays can be printed next to each other on a single web and transported through the necessary steps easily because of the flexible substrate. The patterns are defined by conductive traces tens of microns wide, so they could be created by printing a SAM onto a metal-coated substrate and then etching away the unnecessary areas, which works well in a roll-to-roll context. An alternative is to perform direct microcontact printing of conductive liquid ink onto the flexible substrate [11].

1.2.2 Large Area Sensors

Large area sensors are defined by their ability to sense distributed phenomena, as opposed to those from point sources. One area where these are useful is solar panels, where, especially in the desert, dust build-up on the panel is particularly harmful to the production of energy because it blocks solar insolation [12]. The detection of the dust upon the panels is the first problem. However, there is also a need to remove the dust from the panel once it has been detected. Currently, the dust is only detected by loss in energy generation and must be removed manually with water, a scarce resource in the desert where many such panels are located. This brings about two potential applications for large area printed electronics: a sensor that can sense the quantity of dust present on the panel, and an actuator that can transport the dust off the panel. The latter is demonstrated in Mazumder’s work on electrodynamic screens for dust mitigation on solar collectors [13]. Indium tin oxide (ITO) electrodes deposited on PET substrate powered by a three phase power supply were used to block dust deposition [14]. The electrodes had features on the order of 100µm, which are easily within the resolution range of microcontact printing.

Another large area sensor of interest is a long range gesture and acoustic human-machine interface. This interface would be a distributed array of microphones and capacitive sensors which can be attached to a surface like wall paper [15]. This would be use in collaborative workspaces where multiple speakers wish to vocally interface with a computer. The array of microphones can be used to process the cacophony, localize the speakers, and identify what each speaker is saying. Again, the need is a
large area circuit patterned on a thin film.

1.2.3 Battery Electrodes

Battery technology is an active area of research, especially in regard to thin film lithium ion battery electrodes. A potential improvement to these electrodes would be to pattern vertically aligned CNTs onto the current collector to form the cathode/anode. The CNTs could perform better than state of the art electrodes due to their ‘excellent electrical conductivity, large specific surface area, high mesoporosity, and good electrolyte accessibility’ [16]. Microcontact printing could be used to pattern these electrodes by printing onto CNT growth catalyst and etching away the areas where growth was not desired.

1.3 Barriers to Scale-Up

To date, the bulk of the literature concerns studies of the basic chemistry and transfer physics of the microcontact printing process with little attention paid to scale-up issues [17]. The chemistry of the thiol inks and the surface characterizations are well documented and considerable work has been done on producing small, flat micro-patterned stamps [7]. However, recent work has demonstrated the possibility of roll-to-roll printing at speeds up to 400ft/min, though it also demonstrated that significant problems with basic stamp production and printing consistency exist at all speeds [18]. Thus, while the process has great potential, there has yet to be a concerted effort at understanding both the fundamental and practical issues involved in a transition to full-scale production.

Earlier work has identified several key issues that are vital to the scale-up of this technology:

• Continuous, uniform cylindrical tooling

• Precise contact region manipulation

• In-process printing measurement
The need for cylindrical tools has been addressed by Petrzelka and Hardt [19] and Nietner and Hardt [20]. These works developed a novel centrifugal casting and cylindrical mask-less patterning method, which created seamless cylindrical PDMS tools. To precisely control the printing contact region, a flexure-based device for roll-to-plate printing was demonstrated by Petrzelka and Hardt [21]. Thereafter, Libert [22] developed a precision print roll positioning system for a continuous roll-to-roll print press. This system, which combines air bearings for linear motion and roll rotation, flexures for roll tilt, and voice coil linear actuators, was used for the majority of the experimentation performed in this work.

1.4 Focus of this Work

The larger context of the work reported here addresses the key issues to enable a large area, high rate microcontact printing process capable of micron-scale patterning a flexible substrate material. At the start of this work, the cylindrical tooling manufacturing machine, as well as the roll-to-roll printing machine, had been built. However, no testing of the complete roll-to-roll printing process had been attempted with this equipment. Furthermore, it was known that an inking system, which had not been included in the original printing press, would be necessary.

Consequently, the focus of this work is on the design and development of the continuous inking system for the roll-to-roll printing machine. In the context of the overall system, this was the main factor required to achieve continuous printing. Hence, the testing of the inking system and the printing system as a whole serves to investigate the viability of scaling microcontact printing.
Chapter 2

Prior Work

2.1 Basics of Soft Lithography and Microcontact Printing

Microcontact printing was developed by the Whitesides group at Harvard University in the 1990’s [23]. The original process required casting a PDMS stamp using a mold created from a wafer patterned using conventional lithography. After curing and removal from the master, the stamp was coated with alkanethiols and dried with nitrogen. The inked stamp was carefully brought into contact with a gold-coated substrate. The alkanethiols transferred from the stamp to the substrate only where contact was made, effectively replicating the pattern of the stamp and the original master.

The printed alkanethiol forms a monolayer on the surface of the gold film. During wet chemical etching, this monolayer only protects the gold underneath the printed pattern, and the rest is removed. In its original form, this process patterned features as small as 1µm [24]. The process was further developed by Biebuyck et al. to reliably cast and print geometry with features below 100nm in size [25]. Figure 2-1 shows this process graphically. Reviews of microcontact printing achievements and limitations are available [1], [3].
Figure 2-1: A summary of the microcontact printing process [5]. The master is patterned, and then the PDMS is cast into it to create a stamp. The stamp is inked and then dried. The stamp is brought into contact with the substrate, transferring the SAM to the surface. Lastly, etching is performed to cut the pattern into the substrate.
2.2 Inks

2.2.1 Molecular Inks

In this work and many others, microcontact printing is performed with molecular inks that form self-assembling monolayers (SAMs). The inks are long chains of organic molecules with functional groups at the head and tail. The head group has affinity for the target metal, creating covalent bonds with the substrate upon contact. However, these head groups do not bond well to the molecules themselves or to the tail groups. As a result, the molecules mainly bond to the substrate, aligning themselves into a monolayer as shown schematically in Figure 2-2. The tail groups can be functionalized to change the interface properties of the monolayer to improve further processing.

![Simplified schematic of SAM on substrate](image)

*Figure 2-2*: Simplified schematic of SAM on substrate [22]. The head group of the molecule, shown in orange, bonds to the substrate. The chains of the molecules align, allowing a dense SAM to form, and effectively changing the surfaces properties to those of the tail group, shown in blue.

Alkanethiols are a subset of SAM molecules with an affinity for gold. In microcontact printing, the stamp is coated with the SAM and then dried on the surface before being brought into contact with the substrate. Upon contact, the alkanethiols on the stamp surface adsorb to the gold substrate. Once the alkanethiols are on the gold, they self-assemble into a monolayer within minutes [26]. While there is some diffusion along the surface, it is generally limited, so the SAM pattern on the substrate is a good replica of the pattern cast into the PDMS stamp.

The alkanethiols transfer to the substrate quickly; as stamp contact times of only 1ms have been shown to successfully reproduce patterns [4]. The short duration of the required contact time is crucial to high speed microcontact printing. Since the
molecules adsorb to the surface from a dry state, fluid dynamic effects are unimportant. Finally, because alkanethiol ink can be absorbed into PDMS and is able to diffuse through it, a stamp saturated with ink could be used for multiple prints before having to be re-inked [27]. Consequently, alkanethiols have become a common and robust solution for microcontact printing on gold substrates.

In addition to alkanethiols, other inks have been used to create SAMs. On gold, as well as palladium, silver, and copper, eicosanethiols have been used. In Geissler et al., these were used to print micron scale patterns [28]. Phosphonic acids, such as octadecylphosphonic acid (ODPA) have been shown to form SAMs on aluminum substrates [29], [30]. Especially with the low cost of aluminum compared to precious metals, this is significant because it could enable roll-to-roll microcontact printing of aluminum-coated PET films.

2.2.2 Liquid Inks

Microcontact printing can also be used to print liquid inks. In electronics, it is important that the patterned traces be conductive. With SAM inks, this is achieved through selective etching of conductive substrates. To create these traces with liquids, conductive liquid inks are printed directly onto non-conductive substrates in the desired pattern, as shown in Hale’s work (Figure 2-3) [11]. Especially compared to the metalized substrates required in SAM printing, this provides reduced cost and increases flexibility. Polyethylene terephthalate (PET) films have emerged as common substrates in the printed electronics industry due to their low cost, high clarity for use in displays, and ease of handling in roll-to-roll machinery. A review of the use of conductive liquid inks and polymer substrates used in microcontact printing is provided by Kaufmann and Ravoo [31].

However, as a result of the liquid transfer process required with these inks, the fluid dynamic interaction of the stamp, ink, and substrate are important. Because of the complexity of this interaction it is currently not well understood, especially compared to printing with SAM ink. Hale’s thesis work addressed some of the key important printing parameters necessary with liquid inks [11]. This highlights the
Figure 2-3: Microcontact printing of conductive liquid ink onto polymer substrate by Hale [11]. Using a PDMS stamp, Cabot CSD-66 silver nanoparticle ink was printed onto a cyclic olefin copolymer substrate, showing crisp lines at micron scale.
sensitivity to ink fluid parameters, and stamp and substrate surface energies.

2.2.3 Ink Selection

While there are a large variety of inks that can be used in the microcontact printing application, the goals of this project were to use ink, not to develop ink. Consequently, it was desirable to pick a robust and easy-to-use ink for the target substrates. The combination of HDT and ethanol for ink with gold-coated substrate is very well studied, which made it an attractive option. The most important factor, however, was the work of Helmuth et al., which showed complete SAM formation in as little time as 1ms with this combination [4]. At the anticipated print speeds, contact times as low as 0.1s we expected, so the relatively quick SAM formation of HDT would work well in the roll-to-roll context.

The main drawback of HDT was its lack of compatibility with traditional potassium iodide/iodine (KI/I$_2$) gold etchants. This issue was solved with a custom etchant formulated from thiourea and ferric nitrate. Initial tests of printing and etching with this system confirmed that it worked robustly and would be useful in the context of this experimentation. A very similar alkanthiol, mercaptohexadecanoic acid (MHDA), was also selected for initial testing because it is compatible with KI/I$_2$ gold etchants. However, the MHDA did not perform as well when printed with lower contact times, so HDT was used for the remainder of the experimentation.

2.3 Stamps

2.3.1 PDMS Stamps

The stamps using in microcontact printing are typically cast from the thermoset silicone-based elastomer polydimethylsiloxane (PDMS). In this work and many others, the PDMS used was Dow Corning Sylgard 184. To create a stamp, the base elastomer and the curing agent are thoroughly mixed and cast into the master mold. The material then cures in the mold, creating the stamp. Since PDMS does not expand or shrink significantly during curing, it reproduces the master pattern accurately. While not absolutely necessary, the liquid PDMS is often degassed in a vacuum before
casting to remove air bubbles that can create flaws the final stamp.

In addition to the ease of casting PDMS, it is also useful in microcontact printing because of its ability to make conformal contact with the surface. Since SAM transfer occurs mainly through contact of the stamp and the substrate, it is crucially important that the complete area of each feature comes into contact with the substrate. This comes from the material’s ratio of surface energy to elastic modulus. Since this ratio is high for PDMS, the adhesive forces at the surface can easily flex the material into contact with a substrate. Consequently, PDMS stamp features can conform to asperities in the substrate and make conformal contact, as shown in Figure 2-4 [32].

![Figure 2-4: Schematic indicating how PDMS creates conformal contact even in the presence of surface roughness [32].](image)

PDMS also has some disadvantageous traits for microcontact printing, however. Organic solvents, such as the ethanol used in this work, can cause swelling of PDMS [33]. This can cause distortions in the stamp and limit accuracy of pattern replication. Furthermore, because of the high surface energy and low elastic modulus, it is prone to elastic feature collapse, as shown in Figure 2-5 [32]. Since the PDMS is not very stiff, the stamp is prone to deformation under print pressure. This can cause the stamp features to bulge or buckle under the compressive load. Especially in sparsely featured areas of a stamp, this can also cause roof collapse, where the non-feature area of the stamp is pressed down into contact with the substrate. Lastly, closely packed features can laterally collapse, because of the low stiffness, and then stick to each other as a result of the high surface energy. These stamp failure modes must be taken into account when designing stamp patterns, by managing the feature size and spacing, as well as during printing, by precisely controlling the contact interface between the stamp and the substrate.
Figure 2-5: The four major failure modes of PDMS stamps per Petrzelka: (a) sidewall collapse and bulging of features, (b) roof collapse, (c) buckling of features, and (d) lateral collapse [21].

2.3.2 Flat and Wrapped Stamps

Microcontact printing is traditionally a plate-to-plate process, which stems from its lithographic origins. To create the stamp, the pattern master is created with traditional lithography on a silicon wafer. The PDMS is cast onto the wafer, and the stamp is created with the pattern matching the one in the wafer. However, as has been discussed, the small flat stamps created with this method are not useful for a full scale manufacturing process.

One step towards a roll-to-roll process is to wrap these flat stamps around a cylindrical print roll. Xia et al. performed roll-to-plate printing in this manner by wrapping a flat stamp around a hand roller and printing on silicon wafer substrates [34]. While this showed microcontact printing could work in a roll-to-plate setting, it also highlighted the issues associated with wrapping a flat stamp onto a cylindrical roll. First of all, these stamps are inherently limited by the size of the wafers on which they are made. Secondly, they are limited by how well they can be mounted to the roll, as was also seen in Datar’s work [35]. Not only does wrapping the stamp distort the features, it also inherently leads to a seam where the two ends of the stamp meet. This seam creates a large disturbance in the contact with the substrate during printing, as the seam is significantly larger than the stamp feature height. It introduces disturbance into the printing process every revolution and prevents the printing of patterns that are large than one stamp circumference.

2.3.3 Cylindrical Stamps

Because of the issues involved with wrapping flat stamps, a true roll-to-roll process requires cylindrical stamps. While cylindrical tooling does not inherently solve the mounting issues, it does alleviate the distortion problems and seam associated with
wrapping the flat stamp. To create these tools, Petrzelka developed a centrifugal casting machine [32]. This machine utilizes a rotating drum into which photoresist is cast and then patterned with direct write lithography. Once the master pattern is created, liquid PDMS is cast into the drum and spun during curing to create a cylindrical stamp which has no seam. The machine is shown in Figure 2-6.

![Figure 2-6: Close up view of the casting drum from Petrezelka's centrifugal casting machine. A stamp made with the machine can be seen with features (white arrow) matching those seen inside of the drum (black arrow) [19].](image)

Due to the high surface energy of PDMS, it is very difficult to slide along a metal print roll. To address this, a specialize air bearing was created to mount the stamps onto the metal print roll. The air bearing, shown in Figure 2-7, channels air between the stamp and the metal, which lubricates the interface, allowing the stamp to be slid along the roll. Once in place, the stamp is pinched off the air bearing and the adhesion of the stamp keeps it stuck to the roll after the air bearing is removed.
Figure 2-7: The air bearing used to enable mounting of cylindrical stamps on metal rolls despite the adhesion of PDMS to the roll [32]. The device creates a lubricating film of air between the stamp and the roll, which allows the stamp to slide from the end of the roll (a) onto the roll (b).

2.4 Printing Machines

2.4.1 The Stagnaro Machine

The need for roll-to-roll microcontact printing equipment stems from the desire to scale microcontact printing to a high speed, large area process. The beginning of this work stems from a project performed in collaboration with NanoTerra. Stagnaro developed a web handling machine for continuous printing using a PDMS stamp, as shown in Figure 2-8 [18]. The stamp was a flat stamp wrapped around a large diameter print roll, which created the first major issue for the machine, as wrapped stamps inherently cause large disturbances to the print force because of the seam. Furthermore, mounting the stamp on this machine was difficult, and results depended on operator skill [35]. In this machine, the print force was not directly controlled. Instead, the displacement between the print and impression rolls was precisely adjusted, and the deformation of a foam spring between the two rolls determined the force involved. As this did not directly control print force, the contact was not robust to system disturbances. However, the Stagnaro machine did successfully print 40μm features at speeds of up to 400ft/min using HDT ink and gold-coated PET substrate. This machine reinforced the need for continuous, uniform cylindrical tooling and equipment for precise contact region manipulation.
Figure 2-8: The Stagnaro machine: a roll-to-roll microcontact printing machine built in collaboration with Nano Terra, Inc. [18]. Although this machine printed at web speeds of up to 400ft/min, its wrapped stamp and fixed print roll made the printing prone to disturbances and errors.
2.4.2 The Petrzelka Machine

Petrzelka built a precision roll-to-plate microcontact printing machine to investigate this type of printing. The machine, shown in Figure 2-9, could utilize either force or displacement control of the stamp during printing [21]. The substrate was mounted to a stage which pushed it through the machine as the stamp rolled freely over it. This type of contact is different from plate-to-plate because only part of the stamp is in contact with the substrate, and that contact zone propagates along the stamp as it rolls. The experimentation performed with this machine showed that precise control of the contact region was indeed necessary. This was accomplished through in-situ inspection of the stamp contact with the substrate, and was fed back into real-time control.

Figure 2-9: The roll-to-plate microcontact printing machine built by Petrzelka [32]. The print roll is guided by flexures and actuated with voice coils in two degrees of freedom: height and tilt. The linear stage underneath controlled the motion of the substrate during printing.
2.4.3 The MIT Machine

As a follow up to the Petrzelka machine, Libert and Nill built a complete roll-to-roll web handling machine with precision print head, which is shown in Figure 2-10 [22]. This machine uses off the shelf components to create a web handling system combined with a fully custom precision print head, pictured in Figure 2-11. The web is routed through the web handling section to the large diameter impression roll where the print head brings the stamp into contact for printing, as shown in Figure 2-12. This print head is capable of manipulating a 15cm wide print region with position resolution below 100nm and force resolution of 0.02N. Machine characterization showed accurate web speed and tension control, as well as repeatability of the printing head actuation. However, due to the limitations of the in-situ inspection bandwidth, complete closed loop print head control was not implemented. In light of this, open loop force control of the print head was used for printing on this machine in this thesis.

2.4.4 The CUHK Machine

A group at the Chinese University of Hong Kong (CUHK) also recently developed a precision flexure-based roll-to-roll machine [36]. Unlike the MIT machine, this one has many more degrees of freedom to align the various components, but the central components of web handling and printing on a large impression roll are similar. This machine was characterized to nanometer positioning accuracy and 0.05N force control. It successfully printed hex patterns in the tens of micron scale range, as well as 600nm optical gratings, shown in Figure 2-13.
Figure 2-10: The roll-to-roll microcontact printing machine developed by Libert and Nill [22]. The web handling rolls can be seen on the left, with the web stretching over the central impression roll. Printing occurs between the impression roll and the precision print head assembly, seen at the right.
Figure 2-11: The precision print head built by Libert [22]. The print roll is supported by air bearings for frictionless rolling. Each side of the roll is supported on a linear air bearing slide and actuated with a voice coil to enable longitudinal and slewing motion of the roll.

Figure 2-12: A schematic cross section of the print interaction between the stamp and the substrate as it passes over the impression roll [22]
Figure 2-13: An SEM micrograph of an optical grating printed by Zhou et al. [36]. The lines are 600nm wide, and it can be seen that the edges are not very crisp.
Chapter 3

Inking System Design

3.1 Overall Project Goals

The main goal of this work was to show the scalability of microcontact printing to a large area, high throughput roll-to-roll process. This required building on the work of Stagnaro, Petrzelka, Nietner, Nill, and Libert, and utilizing the cylindrical tooling and roll-to-roll printing equipment to perform continuous microcontact printing. The centrifugal casting machine already demonstrated its ability to make functional tools. Though the web handling and print head capabilities of the roll-to-roll printing machine had been characterized, it had not yet been used to perform microcontact printing. The roll-to-roll printing that had been performed by the Stagnaro machine was not continuous, for the ink was manually applied to the stamp. Hence, it was necessary to add an automatic inking mechanism to the printing press and perform continuous roll-to-roll printing.

The goals of print quality and rate were set largely based on the tooling available from the centrifugal casting machine. The stamps used in this experimentation were made up exclusively of circumferential line features 30µm wide on a 100µm pitch. Furthermore, the stamps had a maximum width of 2in of featured area. Hence, the input variables for rate and quality were narrowed to web speed and line quality. The web speed goal was set to 5in/s, a relatively high speed for the lab scale printing press, and a speed that could yield significant throughput, especially at higher web widths.
For the printed lines, the primary goal was to have successful pattern replication without major stamp failures such as roof collapse. There was also desire to have minimal variation in line width, as well as no line break defects.

### 3.2 Inking System Concept

#### 3.2.1 Traditional Inking Strategies

The first step in designing the inking system was to investigate traditional inking strategies used in microcontact printing. Largely, inking had been based on soaking the stamp in the SAM ink before printing. This is because many thiols, including HDT, diffuse into the PDMS during soaking and then diffuse out during printing. However, this strategy does not make very much sense in a continuous roll-to-roll application, as the printing would be limited by how the stamp absorbed ink during printing. Many diffusion inking techniques used multiple days of soaking to ensure saturation, which is unacceptably long. Lastly, the swelling of the stamp caused by saturation with organic solvent is undesirable.

The two other common inking strategies are wet inking and contact inking [37]. Wet inking is performed by applying bulk liquid ink onto the face of the stamp. The bulk liquid is then evaporated, leaving a film of SAM on the stamp surface. Alternatively, in contact inking, the bulk ink is placed on an unpatterned PDMS ‘ink pad.’ Once the excess is dried off, the stamp is put in contact with the ink pad, so the surface film of SAM transfers to the features of stamp. It is important to note that in the latter method, only the features of the stamp in contact with the ink pad are inked; unlike wet inking, where the entire stamp surface is inked.

Some initial printing was performed by manually placing the stamp in contact with the substrate. For these tests, the stamp was swab-inked, which is a modification of wet inking. Instead of dropping bulk liquid on the stamp, a thin liquid layer is applied with a foam swab. This has the same effect as traditional wet inking, except that it is less wasteful and the liquid evaporates more easily. It is also much more convenient for inking cylindrical stamps, as the ink does not flow everywhere. Comparisons between
swab inking and the bulk liquid inking showed no obvious difference in printing results. This testing indicated that applying liquid ink to the surface of the stamp and then drying it created good prints. To adapt this method to the continuously rotating stamp, a method of applying the liquid was needed, as well as a method of drying it. A controlled flow of air was a rather obvious solution to the drying issue, but the question of wetting was more open. Two methods were investigated: spraying the ink onto the stamp as an aerosol, and submerging the bottom part of the stamp in a pool of ink.

### 3.2.2 Aerosol Concept Evaluation

The aerosol inking concept was that the SAM ink would be sprayed as a mist onto the surface of the stamp, creating a uniform film of ink on the stamp similar to spray painting. The ink would then be dried and printed as normal. The initial evaluation of this concept was done with a Central Pneumatic airbrush (PN: 69492), shown in Figure 3-1. The ink was loaded into the paint cup and sprayed onto the stamp. The stamp was then manually brought into contact with the substrate to create the print. These prints were then chemically etched to visually capture the quality of the printed results.

The ink used for these tests was 15mM MHDA in ethanol. The airbrush was run on compressed air at 30psi, the maximum pressure for this airbrush. The stamp was held approximately 6in from the airbrush, and ink was sprayed on in a sweeping motion at full throttle for 2-3s. This did not form a visible film on the surface of the stamp, nor was the stamp wet to the touch. The stamp was then dried with compressed air for 10s before printing. Printing was achieved by manually bringing the stamp into contact with the gold-coated PET substrate for 10s. The samples were then etched with $K I_2/I_2$ etchant, diluted 3:1 with deionized water, for 1min.

Figure 3-2 shows one such print, and it is readily apparent that the print quality is inadequate. The pattern reproduction is poor, and the lines can barely be described as such. The entire print appears to be created from an array of blotches. This is likely as a result of the individual aerosolized droplets of ink contacting the stamp
surface and drying there instead of forming a layer which spread uniformly over the stamp features. In an attempt to make the inking of the stamp more uniform, ink was sprayed onto the stamp until a film of wet ink was visible. Figure 3-3 shows a print created in such a manner, and the results, though better, are still poor. The lines are still formed of blotches of ink, and the line width is inconsistent.

Figure 3-1: Photograph of the Central Pneumatic airbrush used in initial airbrush testing
Figure 3-2: Print from initial aerosol inking testing showing blotchy lines. Inking of 15mM MHDA was performed with 2s of airbrush spray and manually printed. 1min $K_I/I_2$ etch performed to aid visualization.

Figure 3-3: Print from initial aerosol inking testing showing best lines achieved with this method were still unacceptable. Inking of 15mM MHDA was performed with 2s of airbrush spray and manually printed. 1min $K_I/I_2$ etch performed to aid visualization.
3.2.3 Tank Concept Evaluation

The tank concept centers around the idea that submerging a portion of the stamp in liquid ink while it is rotating will completely coat the stamp features in ink. The first test of this theory was done without SAM ink, but instead just the ink solvent base, which has almost identical fluid properties. A tank was 3D printed (Figure 3-4, filled with isopropanol and placed under the stamp on the printing press. It was immediately apparent that the surface energy of the PDMS caused the solvent in the tank to form a meniscus with the stamp. This meniscus was stable even during rotation of the stamp, indicating that the liquid would likely be capable of staying in contact with the stamp during continuous printing.

![Figure 3-4: The 3D printed prototype ink tank](image)

The next test was to actually print with the prototype tank. The tank was filled with 15mM HDT in ethanol, and printing was performed on gold-coated PET with 6N of print force at 0.1in/s web speed. It was not clear whether the section of the stamp coming out of the ink tank was wet with ink, or whether natural convection was drying it well enough. A hand-held air nozzle was used to dry the stamp while it was turning to ensure the ink was dry before contact with the substrate. The samples
from this test were etched in ferric nitrate/thiourea for 1min for visualization. Figure 3-5 shows one such print, indicating good pattern replication.

![Figure 3-5](image)

**Figure 3-5:** Print from initial continuous inking testing done with prototype tank, 15mM HDT, and manual drying. Though there are scratches and missing line segments, overall pattern replication is good. Print force was 6N and web speed was 0.1in/s with a 1min chemical etch to aid visualization.

### 3.2.4 Concept Selection

Based on the comparison between the prints from the aerosol and tank inking prototypes, the concept selection was obvious. The prints from the tank prototype were already comparable quality to the manual printing done beforehand, while the aerosol prints were clearly lacking. The tank concept would need improvement and a real drying system, but the aerosol system would need much more. More thorough understanding of aerosol flow would be necessary to develop a spray which uniformly coated the stamp in ink. Furthermore, the ink spray would need to be prevented from contaminating the substrate, and there would be safety ramifications from spraying solvent and thiol into the laboratory environment. Tank inking was selected because it was clearly a simpler path to success.
3.3 Inking System Design

3.3.1 Requirements

After selecting the tank concept, it was necessary to finalize the details of the inking system. The key requirements stemmed from the overall requirements of the project, mainly the line quality and web speed. The inking system needed to provide a complete coating of ink to the surface of the stamp such that all the stamp features were properly inked. Fulfillment of this requirement would be based on the successful pattern replication in the prints. The system also needed to dry that coating of ink completely, such that only dry transfer of SAM, not liquid ink transfer, occurred by the time the section of stamp came into contact with the substrate for printing. Again, inspection of the print would serve as the main metric to see if the ink was transferred wet or dry. While initial testing showed that complete drying was feasible at low speeds with little modification to the prototype, the main concern was whether the inking system would be able to keep up at speeds up to 5in/s.

3.3.2 Ink Tank

From a material compatibility perspective, the 3D printed plastic of the prototype tank was a poor choice. While the ink solvent did not instantly degrade the ABS, some ink did seep through it. The solvents used in the inks would cause no problems for metals. Aluminum was selected for its ease of availability and machining, as well as its softness compared to steel in case it came into contact with the print roll.

The geometry of the tank was selected to achieve submergence of the stamp without requiring a very large amount of ink in the tank. The SAM reagents are rather expensive (MHDA can cost upwards of 1000$/g), so minimizing waste was desirable. However, since the stamp is mounted on the cylindrical print roll, the maximum submergence of the stamp is only its thickness, usually about 0.035in. To ensure the stamp did not touch the tank bottom and that ink could flow underneath it, the depth of the tank was set to 0.075in. This geometry is shown in cross section in Figure 3-6. The width and length of the tank were offset 1/4in around the maximum...
stamp dimensions to give some clearance for mounting error. The total tank volume was 3.4ml.

![Figure 3-6: Cross section CAD image of the ink tank and print roll](image)

However, this tank geometry causes some additional issues. The walls of the tank prevent the print roll from moving very far from the printing position because they will contact the submerged section of the stamp. It is desirable to be able to retract the print roll far away from the impression roll when working on the machine and performing other tasks. Hence, it was determined that the tank would need to be movable in the vertical direction. During printing, the tank would be almost against the print roll, and when not printing, it could be lowered significantly to avoid the clearance issue and perform tasks such as filling ink into the tank. While there are
many options for creating such motion, a guided pneumatic cylinder was selected for its simplicity. It could provide the necessary two positions, as well as the structure to support the tank, since it is so small. Additionally, the printing press was already plumbed for compressed air, so supplying it would be easy.

The stock mounting options from the end of the cylinder to the tank, however, would have required screws inside the liquid-carrying area of the tank. This was undesirable, as it would add unnecessary leakage paths. Consequently, an adapter plate with shims was incorporated, with a few additional benefits. The bolts mounting the tank could now be accessed from underneath, meaning the tank could be serviced without removing the print roll. Furthermore, the shims between the adapter plate and tank would give adjustment of the level of submergence of the stamp. Lastly, an additional groove was cut around the main tank section to catch any overflow that may occur during printing. A SolidWorks image of the tank assembly is shown in Figure 3-7.

![Figure 3-7: Exploded view of the ink tank assembly with components labeled](image)
3.3.3 Dryer

While nitrogen is used in many other works to dry off stamps, it was deemed unnecessary in this case. Since the printing press is in the open air, there already exists some dust contamination from the room. As long as the air in the dryer was cleaner than room air, it would not significantly impact the overall cleanliness. It was practical to use the existing air system in the printing press, since it was already equipped with water traps and desiccant. A separate nitrogen supply could be added later if a higher level of cleanliness was desired.

The dryer assembly requirements were less informed by the prototype testing, so adjustability was important. A uniform drying flow across the width of the stamp was desirable, but the direction of the flow, as well as the needed flow rate were less clear. The drying needed to occur after wetting, but before printing. The flow needed to point away from the substrate to discourage any stray ink from contaminating the substrate, but it also need to avoid disturbing the ink in the tank. Schematically, this is shown in Figure 3-6. Since the air flow path could not be exactly predicted without complex analysis, LocLine, adjustable segmented hose, was selected to carry the air to the nozzles.

Since the dryer needed to provide evaporative mass transfer, high air velocity was desirable. Hence, a small exit area of $2 \cdot 10^{-5} m^2$ was used to ensure the flow would be sonic at nozzle exit. The jet would entrain air and decelerate after exit, so moving the nozzle close to the stamp surface would increase performance. This reinforced the decision to use adjustable hose to tune this position. To provide adjustability of the stamp area covered, four 9-hole flat nozzles were used in drying. A single full width flat nozzle was considered, but would not have provided the necessary range of adjustment for the initial design.

3.3.4 Sensing

It was also desirable to measure inking and printing parameters during printing to understand their effects on the system. The printing press itself was already equipped with a variety of sensors [22]. Web speed and print head position were measured,
while web tensions and printing force from the actuators were commanded, but not measured. For the inking system, the main control parameter was the mass flow rate of the dryer. This was controlled and measured with an analog mass flow meter. It was also desirable to measure the amount of ink in the tank. Because of the tiny amount of liquid and correspondingly small tank, no off-the-shelf solutions capable of this measurement were found. It was determined that developing a sensor was not within the scope of the project. Hence, the important parameters measured during experimentation were web speed and dryer flow rate.

3.3.5 Full Assembly

After assembling the ink tank and dryer assemblies, a few adjustments were necessary. As intended, the ink tank was shimmed such that the top of the tank was just below the print roll, giving maximum submergence for the stamp. The nozzles were also adjusted. The angle was set such that the flow was nigh tangent to the surface of the roll and did not disturb the ink in the tank. The proximity to the stamp was set such that the flow created an air bearing effect: a finger placed where the flow impinges would be repelled from touching the stamp. The four nozzles were arranged so that this air bearing effect was uniform across the width. Pictures of the completed assembly are shown in Figures 3-8 and 3-9. Figure 3-10 shows the static meniscus formed between the stamp and the fluid in the tank, which was dyed blue for easy visualization. Figure 3-11 illustrates the flow of ink present on the stamp as a function of web speed. The dyed ethanol is used to show how little ink is present on the stamp surface at low speeds, while there is a large liquid flow on the stamp at high speeds. The presence of this liquid flow indicates that the drying system is very close to the limit of being able to effectively dry all the ink on the stamp before the print zone.

Initial dryer testing at full air flow dropped the main pressure regulator from 80 to 65psi. To accommodate the high flow rate of the dryer, the main supply line was shortened, the on-machine distribution was converted from a series of junctions to a single manifold, and the lines for the dryer were all converted to 1/4in. This upgrade reduced the main regulator pressure drop to only 5psi with the dryer flowing at 6scfm.
Figure 3-8: Overview of the inking assembly installed on the roll-to-roll printing press

Figure 3-9: Side view of the inking assembly installed on the roll-to-roll printing press showing the proximity of the drying nozzles to the surface of the stamp
Figure 3-10: Close up image of ink meniscus. Blue-dyed ethanol was used to illustrate the fluid interaction of the ink with the stamp submerged in the tank.
Figure 3-11: Comparison of ink flow on stamp at different web speeds with 6 scfm dryer flow. At low speed (a), there is very little visible ink on the stamp surface because it is dried so quickly. At 1 in/s (b) there are a few drops visible flowing down the stamp, but at 4 in/s (c) there is significant fluid flow down the stamp surface.
Chapter 4

Experimentation

4.1 Goals

The core experimentation performed in this thesis served two main purposes. The first was to demonstrate functioning continuous microcontact printing, and the second was to understand the effects of system parameters on the print uniformity and defects in the printed product.

To meet the overall project goals of printing at manufacturing speed, it was logical to attempt to print at the highest web speed possible while still retaining acceptable print quality. In line with the focus on continuous inking, the expectation was that the inking mechanism would be the limiting factor on printing rate; specifically, the capability of the dryer to effectively evaporate the ink solvent from the stamp before contact. In these high speed runs, the quality measurement was the key factor in determining whether the prints were successful.

In addition to high rate, repeatability was also of prime concern. Especially with the cylindrical tooling, it was desirable to determine whether the prints were consistent when performed under the same circumstances with the same area of the stamp. The stamps had identifying features and defects in them, so comparing both the good areas and the defective sections shed light on how consistently the system performed from one revolution to the next.

Lastly, it was important to demonstrate that the system, especially the inking
system, could perform for extended print lengths. It was necessary to understand whether there would be ink excess or deficiency on the stamp as a result of running the system for many revolutions of the stamp.

4.2 Methods

4.2.1 Experimental Parameters

The experimentation performed can be broken down into a few main processes: material preparation, inking and printing, and etching. The experimental goals focused entirely on the effects of the inking and printing processes on the print output. The material preparation and etching steps were necessary to achieve the result, but were intended as constants.

First, the ink, the substrate, and the stamp were prepared. The parameters associated with this were the ink concentration, substrate material and thickness, and stamp pattern. For these experiments, these parameters were all kept constant. In the inking step, the method of applying the ink to the stamp, as well as drying it once on the stamp are crucial parameters and served as the key independent variables in these experiments. During printing, the web tension, web speed and print force can be varied on the printing press. Because of the large wrap angle around the impression roll, web tension does not heavily affect the web during printing. Web tension was kept minimal to avoid excessive strain in the web, but high enough to convey the web without slack. A standard print force of 6N, 3N per side, was used. The web speed was an independent variable. During the etching phase, the etch bath concentration, etch time, and rinse time could be varied. As the etching is performed purely to allow for visualization, once a combination of these parameters which resulted in good microscope pictures was found, these were also kept constant. Table 4.1 summarizes this information.
Table 4.1: Summary of Experimental Parameters

<table>
<thead>
<tr>
<th>Experimental Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Web Speed</td>
<td>Varied</td>
</tr>
<tr>
<td>Web Tension</td>
<td>2lbf</td>
</tr>
<tr>
<td>Print Force</td>
<td>6N</td>
</tr>
<tr>
<td>Ink</td>
<td>15mM HDT in ethanol</td>
</tr>
<tr>
<td>Drying Flow</td>
<td>Varied</td>
</tr>
<tr>
<td>Etch Bath</td>
<td>0.1M thiourea and 0.01M ferric nitrate</td>
</tr>
<tr>
<td>Etch Time</td>
<td>2min</td>
</tr>
<tr>
<td>Rinse Time</td>
<td>1min</td>
</tr>
</tbody>
</table>

4.2.2 Procedure

Ink

The three main elements of the print are the ink, the stamp and the substrate. The ink itself was prepared to a concentration of 15mM Hexadecanethiol (HDT) in ethanol. This was achieved by weighing out the solid HDT into a beaker, and then filling the beaker with ethanol to about 3/4 of the required amount. This mixture was stirred with a ceramic stir bar at 50°C on stir setting 8 for 5min to dissolve the HDT. The solution was then poured into a graduated cylinder, and ethanol was added to reach the desired liquid amount, and hence the desired ink concentration. The ink was then transferred to scintillation vials until it was used. The mixed ink, as well as the HDT reagent, were stored in a freezer as recommended by the manufacturer.

Stamp

The PDMS stamps used were manufactured in the lab’s centrifugal casting machine. PDMS attracts dust readily, so the stamps were stored inside petri dishes to help protect them against general contamination. Before and after printing, each stamp was cleaned with the solvent appropriate for its ink type. This was intended to remove any excess ink from the stamp surface. For stamp 313, the one used for the HDT experimentation discussed here, this solvent was ethanol. To clean it, the stamp was rinsed with ethanol and left to air dry.

The stamp was mounted to the print roll using the custom air bearing shown in
Figure 2-7. The stamp was placed onto the air bearing, and then the stamp and air bearing were placed over the print roll. The air flowing through the bearing and under the stamp kept the stamp from sticking to the roll. Once in the correct location on the print roll, the stamp was pinched off the air bearing so that it contracted and seated onto the roll. The same processes was performed in reverse to remove the stamp after printing.

**Inking**

As explained earlier, the crucial steps of inking are to provide liquid ink to the surface and then dry off the solvent. During initial testing and development, swab inking was the method of choice. Foam covered Puritan swabs were used to transfer ink from the scintillation vial to the surface of the stamp. Wiping the wet swab on the stamp created a thin layer of ink on the surface. This was then dried off using dry shop air before printing.

During the structured experimentation of the continuous inking system, the inking process was largely automated. Once the stamp was mounted, ink was filled into the tank with a transfer pipette. The tank was then raised to check if the ink level was high enough to form a meniscus with the stamp. If not, ink was added until the meniscus formed. If so, the system was ready for printing.

**Substrate**

The substrate used in the experimentation was 0.1mm PET coated in 20nm of pure gold. It was stored rolled up inside a plastic bag to avoid general dust contamination and always handled with gloves. As the substrate is 3in wide, while the stamp is only 2in wide, the substrate was cut down the middle before printing, forming two 1.5in wide strips to conserve material.

Because of its value, the gold-coated substrate was not used as the web in the printing machine. This would have required large sections of substrate to reach from the unwind roll to the rewind roll, of which very little would actually be used in the print. Instead, uncoated PET was wound into the machine and the gold-coated

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1This material was donated by Nano Terra, Inc. 737 Concord Ave. Cambridge, MA 02138.
substrate was taped to it for printing. This enabled use of only the necessary amount of gold while still enabling roll-to-roll printing. The substrate was taped to the transport web 5in back from the contact zone such that almost one revolution of the stamp would be completed before the printing began.

**Printing**

The printing itself was entirely autonomous. Once the stamp was mounted, the substrate taped to the web, and the ink loaded into the tank, the machine was ready. Before running, the web tension, web speed and printing force were set in software. With the open loop print force system, there was some uncertainty in the uniformity of the print force distribution. Consequently, the desired print force settings were usually visually checked by looking at the stamp contact with the impression roll to ensure complete contact. If it was obviously more compressed on one side than the other, the print force settings were adjusted. Once the machine parameters were set in software, the dryer was turned on to the desired flow rate. Then the print force actuators were enabled, and finally the web transport was activated.

During printing, no operator input was required, so it was a good opportunity to observe the machine. It was useful to watch to ensure the web remained properly tensioned and the inking system was functioning properly. Once the gold substrate passed through the printing area, the machine was stopped. The substrate was un-taped from the transport web and moved to further processing. Finally, the stamp was removed for cleaning and storage.

**Etching**

The main form of post-processing of the prints was wet chemical etching. The goal of this was to etch away the gold in the areas of the print not covered in HDT to create contrast when the print was viewed under a microscope. This required mixing the etchant, immersing a sample of the print in the etchant for some time, and then immersing the sample in water to stop the etching process. The print, which is 1.5in wide, was cut into 1in long samples to easily fit into a 50ml beaker. The etchant of choice was a solution of 0.1M thoriurea and 0.01M ferric nitrate in water.
The etchant was created by weighing out 0.61g thiourea and 0.32g of ferric nitrate nonahydrate into a 50ml beaker. This was then filled to 40ml with deionized water and stirred with a ceramic stir bar until the reagents were visibly dissolved, which took around 2min on stir setting 8.

The etching itself was performed by holding the print sample with tweezers inside the 50ml beaker full of etchant. After some trial and error, it was determined that a 2min etch time gave good image contrast, so that was used for the majority of the experiments. After the time in the etch bath, the substrate was moved to a beaker full of water, where it was held for another minute to stop the etching.

4.3 Image Processing

After etching, an LW Scientific LW200 transmission microscope equipped with an AmScope MU1000 digital camera was used to visualize and capture the prints. However, a microscope image does not provide a concrete method of comparison to other prints. Digital image processing was a useful tool for providing quantitative evaluation of the prints. Since all prints performed were of the same pattern, a simple algorithm was created in MATLAB to measure the quality of the printed pattern. This algorithm measured the width of the lines and found line defects so the line width variation could be quantified and compared among prints. This process can be summarized as follows.

1. Pre-Processing

   (a) Convert image to grayscale and invert coloring
   (b) Calculate and remove image background
   (c) Crop image edges
   (d) Convert image to black and white based on threshold
   (e) Rotate image to make lines horizontal

2. Processing and Measurement

   (a) Locate centerlines
i. Collapse image to one dimension transverse to lines

ii. Perform peak detection

iii. Calculate peak centers based on width

(b) Measure each line width along its length

i. Create measurement region around centerline

ii. Measure line width at each axial location

iii. Identify regions of anomalous line width

4.3.1 Pre-Processing

The first part of the algorithm was to make the color microscope image into something that could be effectively processed. For the measurement steps to work effectively, pre-processing was required to output a black and white image of only the printed lines with the axes of those lines oriented horizontally. The first step was to convert the image to grayscale and invert it. To help compensate for irregularities in the microscope such as dust and lighting non-uniformity, a background image was calculated and removed from the main image. This background removal combined with cropping the outer 10% of the image, where the lighting was least uniform, gave better overall contrast. The grayscale image was then thresholded into a black and white image using the default MATLAB settings. Lastly, the image was rotated to make the lines horizontal to within 0.1°. To achieve this, edge detection was performed on the black and white image. Then using only the edges, a Hough transform was used to determine the most likely angle at which the image was rotated from horizontal. Then, the image was rotated to correct this error. Figure 4-1 illustrates the results of this process.

4.3.2 Processing and Measurement

The main image processing algorithm aimed to carefully quantify the line width and variation thereof. The width of each line in the image was to be measured along its length. The first step of the algorithm was to find the lines. To do this, the image was averaged along the axes of the lines, effectively collapsing the image to one dimension
perpendicular to the lines. This created an array with peaks where the lines existed, and valleys where they did not, as shown in Figure 4-2. Peak detection was performed on this array to determine the transverse location of each line. Next, the width of each peak was measured and its center located. At this point, the number of lines in the print had been determined and a centerline identified for each one.

Next, the full image was processed using the centerline information. For each centerline, a region slightly larger than the anticipated line size was defined in which measurement should take place. In that region, the width of the line was measured by counting the number of white pixels, as shown in Figure 4-3. The measurement was performed at every pixel along the axial length of each line, so a high density dataset of width information was created. Though the mean and standard deviation of the line width were calculated for each line, it was also desirable to analyze defects. The most common defects seen were line width anomalies, where the line width changes drastically from its mean value because of under- or over-inking, dust particles, tool defects, or poor contact. These defects were detected as areas along the line where the width varied by more than 10% from the mean. With this algorithm, a series of pictures from one print effectively measured many lines along their lengths. It quantified average line width, the standard deviation of the line widths, and percentage of line length that contained anomalous line width.

Figure 4-1: Comparison between the microscope image and results of the pre-processing algorithm used in image processing. Note the image is cropped, straightened, and inverted into black and white, but the line edge defects and broken line defects are still visible.
Figure 4-2: Average values along the length of the lines from picture in Figure 4-1. A value of 1 indicates white, meaning the peaks indicate line locations.

Figure 4-3: Schematic diagram of the line width measurement strategy. Once the centerline is identified, the rectangular region around it is created for measurement. At each pixel along the line length, the number of white pixels in the transverse direction across the measurement region is counted to determine the line width.
4.4 Initial Testing

In the initial stages of system setup, the above procedures were still being developed. The goal at the time was to determine the functional ranges for process variables such as etch time. Prints were manually swab-inked and some even printed by manually pressing the stamp against the substrate. Once the continuous inking system had been installed, it underwent some iteration as well before the experimental procedures were finalized. This testing period defined the baseline of a successful print. Figure 4-4 shows a grayscale micrograph of one of the first HDT prints created on the roll-to-roll printing press. This was swab-inked and printed with 6N of print force at 0.1in/s web speed. The complete pattern replication and well-defined lines with minimal line defects became the goal of all future prints.

![Grayscale micrograph of an initial print of HDT on gold. The dark bands are gold, while the light sections are the transparent PET substrate. The print was roll-to-roll printed using swab-inked 15mM HDT at a print force of 6N and web speed of 0.1in/s. Chemical etch of 1min was performed to aid visualization.](image-url)

**Figure 4-4:** Grayscale image of an initial print of HDT on gold. The dark bands are gold, while the light sections are the transparent PET substrate. The print was roll-to-roll printed using swab-inked 15mM HDT at a print force of 6N and web speed of 0.1in/s. Chemical etch of 1min was performed to aid visualization.
4.5 Web Speed and Drying Flow Experiments

While initial testing of the printing and inking system showed that it was functional, it was important to understand the effects of rate on the printing performance. The two system parameters of choice for this experimentation were the web speed and the dryer flow rate. The web speed affects both the contact time of the stamp during printing as well as the amount of time the dryer has to properly evaporate the ink, and it was hypothesized that significant increases in web speed would necessitate similar increases in dryer flow rate to appropriately dry the ink.

4.5.1 Qualitative Results

The first set of experiments to evaluate this aimed to broadly characterize the ranges of acceptable web speed and drying flow parameters. Seven 12in sections of gold-coated PET were printed at 6N print force. These experimental parameters and results are summarized in Table 4.2. The slowest web speed of 0.25in/s was similar to the initial testing of the system, so there was little doubt that the ink would be properly dried. All three drying settings (2, 4, and 6scfm) were tried, and etching of samples A1 and A3 indicated printing performance was satisfactory: the stamp pattern was well replicated, and there were few breaks in the lines. Images of etched samples are shown in Figures 4-5 and 4-6. Since the ink in sample A3 was properly dried, it was assumed the results from A2, which had higher drying flow, would also be acceptable, so it was not etched and imaged.

All three drying flows were also applied to the 1in/s web speed tests. As shown in Figure 4-7, at 2scfm (Sample A6) the print quality was significantly reduced as a result of insufficient ink drying. The lines are significantly wider and have much rougher edges than the other prints. There are also large smears of ink across the print. At 4scfm (Sample A5), however, the print quality returned to normal, so the 6scfm print (Sample A4) was also assumed to be successful.

When testing at the highest web speed of 4in/s, it was apparent that the drying flow could barely keep up. There was significant flow of liquid ink out of the tank
up the stamp surface as it was rotating to the drying flow, similar to Figure 3-11 (c). At the lower settings of 2 and 4scfm, the ink was still so wet when it reached the substrate that liquid flow onto the substrate was obvious. Consequently, only the high drying flow of 6scfm (Sample A7) was used. When printing this sample, no bulk liquid transfer to the substrate was observed. Etching of the sample revealed areas of successful printing, as shown in Figure 4-8. All samples were etched for 2min in the solution of 0.1M thiourea and 0.01M ferric nitrate followed by a 1min rinse in a water bath.

**Table 4.2:** Web Speed and Drying Flow Experimental Parameters - Experiment A

<table>
<thead>
<tr>
<th>Sample</th>
<th>Web Speed (in/s)</th>
<th>Drying Flow (scfm)</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>0.25</td>
<td>6</td>
<td>Confirmed Successful</td>
</tr>
<tr>
<td>A2</td>
<td>0.25</td>
<td>4</td>
<td>Assumed Successful</td>
</tr>
<tr>
<td>A3</td>
<td>0.25</td>
<td>2</td>
<td>Confirmed Successful</td>
</tr>
<tr>
<td>A4</td>
<td>1</td>
<td>6</td>
<td>Assumed Successful</td>
</tr>
<tr>
<td>A5</td>
<td>1</td>
<td>4</td>
<td>Confirmed Successful</td>
</tr>
<tr>
<td>A6</td>
<td>1</td>
<td>2</td>
<td>Confirmed Failure</td>
</tr>
<tr>
<td>A7</td>
<td>4</td>
<td>6</td>
<td>Confirmed Successful</td>
</tr>
</tbody>
</table>

**Figure 4-8:** Area of Sample A7: Satisfactory printing performance with some visible line edge defects and line breaks, as well as a large misprint near the top of the image. Print was roll-to-roll printed using continuously-inked 15mM HDT and drying flow of 6scfm at a print force of 6N and web speed of 4in/s. Chemical etch of 2min was performed to aid visualization.
Figure 4-5: Area of Sample A3: Satisfactory printing performance with some visible line edge defects and line breaks. Print was roll-to-roll printed using continuously-inked 15mM HDT and drying flow of 2scfm at a print force of 6N and web speed of 0.25in/s. Chemical etch of 2min was performed to aid visualization.

Figure 4-6: Detailed view of Sample A1: Satisfactory printing performance with few visible line edge defects. Print was roll-to-roll printed using continuously-inked 15mM HDT and drying flow of 6scfm at a print force of 6N and web speed of 0.25in/s. Chemical etch of 2min was performed to aid visualization.
Figure 4-7: Detailed view of Sample A6: Heavily defective print showing significantly wider and less defined lines due to liquid ink transfer, as well as smears of ink across the lines. Print was roll-to-roll printed using continuously-inked 15mM HDT and drying flow of 2scfm at a print force of 6N and web speed of 1in/s. Chemical etch of 2min was performed to aid visualization.

4.5.2 Quantitative Results

In addition to the qualitative success or failure criteria, quantitative quality measurement was performed on these samples. For each print, many microscope images were taken to capture the spatial variation of the pattern, and the image processing algorithm was applied to gather quality information. This is indicated schematically in Figure 4-9, which shows how a variety of locations on a print were sampled. The image locations were determined on a print-by-print basis and were selected to illustrate the spatial variation in print quality. Large defects, such as roof collapse or missing contact, were avoided. Figures 4-10 through 4-14 show the average line width, standard deviation of the line width and defect percentage for each line measured in the samples. Each point in the scatter plot is one measured line. Ideally, these points would be tightly packed at a single line width with low line width standard deviations and defect percentages, meaning all printed lines would be the same average width, have low width variation along their lengths, and few line width anomalies.
Clustering like this can be most obviously seen in Figures 4-10 (Sample A1) and 4-14 (Sample A7). While there are some outliers, the large majority of the lines measured fall in the range of 20-35µm with line width standard deviations below 4µm and defect percentages below 10%. In Figure 4-11 (Sample A3), there are two obvious clusters of line widths around 23µm and 32µm. The plot for the under-dried sample A6 (Figure 4-13 indicates significantly higher line width variation, with many lines above 35µm and below 20µm. Additionally, many points are above 3µm line width standard deviation and 10% defect percentage. Figure 4-15 aggregates these metric across the 5 measured prints for comparison. This reinforces the high defect percentage and standard deviation of sample A6, but also reveals a higher average line width.

Figure 4-9: Schematic of microscope images taken of a printed sample. The shaded blue rectangles illustrate the area covered by microscope images, and the size differences occur because some images were be taken at different magnifications.
**Figure 4-10:** Line width scatter plot for Sample A1. There are many outliers in the upper left region, though the remaining line widths are tightly grouped and standard deviations are mostly below 3µm.

**Figure 4-11:** Line width scatter plot for Sample A3. There are two notable line width clusters around 23µm and 32µm. Generally, standard deviations are below 4µm and defect percentages are below 5%.
Figure 4-12: Line width scatter plot for Sample A5. Line widths range widely from 18 to 35µm, but standard deviations are mostly below 4µm and defect percentages are mostly less than 5%.

Figure 4-13: Line width scatter plot for Sample A6. Line widths are highly scattered, though standard deviations are still usually below 4µm.
Figure 4-14: Line width scatter plot for Sample A7. Line widths are mostly clustered between 25 and 35µm with low defect percentages. All standard deviations are less than 5µm, and peak defect percentages are around 25%.

Figure 4-15: Experiment A line statistic comparison. The average line width, standard deviation and defect percentages from all the measured lines in each print were combined to create one data point. The error bars indicate the line width standard deviation. Note the low defect percentages of samples A1, A3 and A5, while sample A6 has a relatively high defect percentage, line width standard deviation, and average line width.
4.5.3 High Speed Tests

In addition to a broad sweep of web speed and drying flow, it was also desirable to push the limits of the system to see the maximum web speed possible. For these tests, the drying flow was set at a constant 6.5 scfm, and a print force of 5N was used. Prints were created at 4, 5 and 6 in/s (Samples B1, B2 and B3, respectively) to capture print quality variation near the limits of the drying system.

Figures 4-16, 4-17, and 4-18 show the print at each of the three speeds. None of them display the usual signs of liquid ink transfer, but the print quality appears slightly degraded, especially for sample B1. The scatter plots in Figures 4-19 through 4-21 show generally wide ranges of line widths. However, there are generally few outliers, and most of the points have defect percentages less than 5%. Figure 4-22 compares the quality of the three prints, and makes it rather obvious that sample B1 has higher average width, line width standard deviation, and defect percentage than the other two samples. This indicates that there is not significant degradation of the print quality as the speed increases.

Figure 4-16: Detailed view of Sample B1: Pattern replication was good and the line edges are sharp; however, there was some spatter on the substrate. Print was roll-to-roll printed using continuously-inked 15mM HDT and drying flow of 6.5 scfm at a print force of 6N and web speed of 4 in/s. Chemical etch of 2 min was performed to aid visualization.
Figure 4-17: Detailed view of Sample B2: Pattern replication was good, but there are many noticeable holes in the lines and a few line break defects. Print was roll-to-roll printed using continuously-inked 15mM HDT and drying flow of 6.5scfm at a print force of 6N and web speed of 5in/s. Chemical etch of 2min was performed to aid visualization.

Figure 4-18: Area view of Sample B3: Pattern replication was good, and there are some broken line edges. Most notable on the third from the top, there are ragged edges consistent with tool defects. Print was roll-to-roll printed using continuously-inked 15mM HDT and drying flow of 6.5scfm at a print force of 6N and web speed of 6in/s. Chemical etch of 2min was performed to aid visualization.
**Figure 4-19:** Line width scatter plot for Sample B1. There are two line width clusters around 25 and 30µm. Some defect percentages in the 20% range are visible, and standard deviations are mostly below 4µm.

**Figure 4-20:** Line width scatter plot for Sample B2. Visibly wide scatter of line widths ranging from 15 to 35µm. Standard deviations are almost exclusively below 3µm, and defect percentages are mostly below 5%.
**Figure 4-21:** Line width scatter plot for Sample B3. Line widths range from 15 to 30µm with most standard deviations below 4µm.

**Figure 4-22:** Experiment B line statistic comparison: The average line width, standard deviation and defect percentages from all the measured lines in each print were combined to create one data point. The error bars indicate the line width standard deviation. Both the mean line width and the defect percentages among the samples vary notably, with Sample B1 having the highest of both.
4.6 Print Consistency Experiments

Another area of interest was the printing consistency. Experiments were performed to compare areas on the prints that were printed by the same section of stamp under the same conditions. These show how the print varies from one stamp revolution to the next with the other parameters remaining constant. Since the stamp has purely circumferential lines, there is one fiducial mark on the stamp which can be used as a clear indicator of location: a transverse break lines across the full width of the stamp. A print from this section is shown in Figure 4-23. In addition to the break in the lines, there are also some ragged edge defects nearby.

![Figure 4-23: Micrograph of the fiducial marking in Sample B2. The break in the lines is due to a lack of feature on the stamp. Ragged edges on the nearby lines, most noticeable on the left, are also due to the stamp.](image)

To check the print consistency, the area nearby the fiducial was inspected and compared at two locations on the prints from the high speed testing. In this particular run, the stamp was apparently mounted to the roll with some slight deformation. As a result, the usually straight fiducial line has some gentle curvature to it. In the following comparisons, it is clear that this curvature is effectively replicated not only
within one print, but also across the three prints. Figures 4-24, 4-25 and 4-26 compare the first and second revolution of the stamp for the aforementioned Experiment B high speed prints. The fiducial line is very similar in all 6 cases, even for some of the smaller details. This is most obvious in Figure 4-25, where the curvature of the fiducial can be seen in both revolutions of the print. Additionally, the ragged edge defects due to improper tool formation are visible in both revolutions, especially in the right side of the images.

Figure 4-24: Side-by-side comparison of pictures from the first and second revolutions of Sample B1. The fiducial mark shown is an indicator of consistent pattern replication. The background contrast difference was a lighting change.

Figure 4-25: Side-by-side comparison of pictures from the first and second revolutions of Sample B2. The curvature of the fiducial mark, as well as the ragged edge defects on the right, are clearly visible in both revolutions.
Figure 4-26: Side-by-side comparison of pictures from the first and second revolutions of Sample B3. The curvature of the fiducial mark, as well as the ragged edge defects on the left, are clearly visible in both revolutions.

4.7 Long Term Inking Experiments

While pattern consistency from one revolution to the next is important, it is also crucial to ensure that the inking system performs adequately over many revolutions. The inking system should fully replenish the ink on the surface every time the stamp cycles through it. However, there are concerns that the ink could either diffuse into the stamp itself or build up on the surface, which could cause insufficient or excessive printing. Consequently, experiments showing printing variations without ink replenishment, as well as during many revolutions of inking are helpful.

Two 18in long section sections of gold were printed at 0.25in/s web speed and 4scfm drying flow with interrupted inking. For Sample C1, one complete revolution of the stamp was printed under usual inking circumstances. After the first revolution, the ink tank was lowered so no more ink would be applied to the stamp, and the print was completed. Figure 4-27 compares an image from the beginning of the print to an image from the end of the third revolution. It is visually obvious that there are significantly more line edge defects and complete line breaks in the later image.

The Sample C2 was printed similarly, except that first the stamp was inked for ten revolutions while in contact with the transport web only. This was to create any ink build up on the stamp were it going to occur. Then, as with the first sample,
one revolution of normal printing on gold was performed, the inking was interrupted, and two more revolutions were printed. Figure 4-28 compares the images from the beginning and end of the print, and again, there are more defects visible on the image from the end section.

![Figure 4-27: Side-by-side comparison of pictures from the first and third revolutions of Sample C1. The third revolution (after inking was stopped) shows a very large number of broken line defects.](image)

![Figure 4-28: Side-by-side comparison of pictures from the first and third revolutions of Sample C2. Compared to Sample C1, the print quality is not notably degraded and, similarly, the later part of the print shows a very large number of broken line defects.](image)

Figures 4-29 through 4-32 show the line width statistics for the two samples at their respective beginnings and ends. By comparing the scatter plots from the beginnings and ends of the prints for both samples, it is clear that the ends of the prints have lower quality. Figures 4-30 and 4-32 have very large scatter of both line width and standard
deviation. Additionally, they have many more points with high defect percentages. This is reiterated in the comparison plot (Figure 4-33), which shows that the prints which occurred after inking had stopped have almost twice the defect percentage and line width standard deviation. Furthermore, there is no clear indication of a difference in quality between the two beginning prints, which suggests the ten revolutions of inking before printing did not affect the print quality.
Figure 4-29: Line width scatter plot for Sample C1-1. Line widths range widely, mostly from 18 to 30\(\mu\)m, but standard deviations are mostly below 4\(\mu\)m and defect percentages are mostly less than 10%.

Figure 4-30: Line width scatter plot for Sample C1-3. Line widths range from 20 to 35\(\mu\)m. Many standard deviations are above 4\(\mu\)m and defect percentages are often greater than 10%.
**Figure 4-31:** Line width scatter plot for Sample C2-1. Line widths vary from 20 to 35µm, standard deviations are largely below 5µm, and defect percentages are mostly less than 15%.

**Figure 4-32:** Line width scatter plot for Sample C2-3. Except 5 outliers, line widths range from 22 to 35µm. Many standard deviations are above 4µm and defect percentages are rarely below 5%.
Figure 4-33: Experiment C line statistic comparison. The average line width, standard deviation and defect percentages from all the measured lines in each print were combined to create one data point. The error bars indicate the line width standard deviation. The trends for the two prints are similar - the printing done after inking had stopped had higher average, standard deviation and error percentage.
Chapter 5

Discussion

The experimentation described in Chapter 4 was intended to show the capability of the system to be scaled to a manufacturing process. Most important to the scalability argument is the roll-to-roll concept, but it was necessary to demonstrate adequacy of the process with respect to speed, quality and robustness.

5.1 Print Speed

While the threshold for ‘manufacturing level’ throughput of printed substrate is not sharply delineated, a goal of 5in/s web speed was set for this project. The contact time of the ink during printing was not expected to be an issue at that speed; rather, the inking system would be the limiting factor. This was confirmed with the initial print testing done with swab inking at up to 1in/s web speeds, as the printing system worked at speed when the ink was applied with a proven method. Figures 4-15 and 4-22 show how the completed system with continuous inking performed under a variety of print speed and drying flow conditions. The most important result is that, when the ink is properly dried, the print quality at the maximum tested web speed of 6in/s is comparable in both line width standard deviation and defect percentage to the low speed (0.25in/s) prints. This indicates that manufacturing level print speed is achievable by the system and the system is not very sensitive to print speed in this range.

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5.2 Print Quality

The quality of the prints performed in this work is not perfect. Large area print defects were caused by two main sources: non-uniform print pressure and wet ink transfer. When print pressure was so high as to cause roof collapse or so low that the features did not even contact, the defects were generally ignored, as this was not important to the inking system. When liquid ink transfer was apparent, the lines, if they existed at all, were malformed over the entirety of the print, as illustrated by Figure 4-7.

As seen in Figure 4-4, one of the best looking prints that was made, there are still a few minor defects in the lines. The pattern replication is clear and the line edges are crisp, but occasionally there is a partial or complete break in one of the lines. These small scale defects, such as line edge roughness, line breaks, and holes, have a few causes. Dust on the stamp or substrate creates small, random imperfections, improperly formed features on the stamp generate ragged edges in the lines, and non-uniform inking creates broken lines where there is not enough ink. These defects were the ones calculated into the defect percentage because they cause line width anomalies. Complete metrology on the stamps has not been performed, but microscope images have shown that some of the lines in the stamps do have ragged edges. However, as shown in Figure 4-23, stamp defects are rather consistently displayed in the prints. Furthermore, cleaning procedures of the stamp, as well as the substrate storage conditions, aimed to keep dust contamination minimal.

The drying flow shows an almost binary effect on the quality of the print, for the ink is either wet or dry when it comes into contact with the substrate. Figure 4-7 indicates rather clearly how the ink flows over the substrate if it is still wet during contact. Such liquid flow completely defeats the dry chemical transfer characteristic of microcontact printing, so it is no surprise that the quality suffers as a result. Instead of creating crisp line edges that replicate the stamp pattern, the ink flows out past the edges of the stamp in an uncontrolled manner. In the situation where there is little wet ink, as in Figure 4-7, this expands the line width and makes the line edges
very rough. With larger amounts of bulk liquid ink, it can flow to the point of coming into contact with the next line, completely covering the substrate in HDT. This was the case in the Sample A4. No quantitative data was generated for these, as the print did not even resemble lines.

Another factor in the quality of the prints which is not significantly varied in this work is the printing force. All of the prints were performed at 3N of actuator force with constant actuator current. Accordingly, the print pressure on the stamp was not known exactly, nor evenly distributed along the width of the stamp. In the most severe cases, this meant some regions of the stamp were not in contact, while others were had enough force to cause complete roof collapse. As the distribution generally varied from lighter pressure to heavier along the width of the stamp, the central section of the stamp generally had the correct pressure to create good quality lines. Most of the microscope images were taken from the corresponding area of the prints, as the outside sections were largely defective from the print pressure variations.

The consistency of the pattern is a crucial indicator of quality and repeatability. The core question is whether a section of stamp always produces the same print. The images comparing printed pattern from one stamp revolution to the next shown in Figures 4-25 and 4-26 indicate exactly that. It is visually apparent that transverse fiducial line appears consistently not only during the multiple revolutions of one print, but also among these three prints. In addition to the fiducial mark, the ragged edge defects in the stamp are apparent in multiple locations nearby. Even these small scale tool defects are repeated among prints. From this, it is apparent that this system provides repeatable pattern replication.

However, the consistently wide range of average line widths displayed in all experimentation is problematic. It does not make sense that the pattern would appear to replicate well, but have such variability when it comes to line width. The answer lies in the stamp itself. While the stamp was not formally measured, Figure 5-1 shows microscope images of two spatially separate sections of the stamp. While it is subtle, the feature widths on the two ends of the stamp are visibly different. This follows from how the lithography system in the centrifuge works, where a gradual
focus change along the width of the stamp could slightly change how the feature is formed [20].

**Figure 5-1:** Side-by-side comparison of microscope images from opposite ends of the stamp used in printing. The image on the right has visibly wider line features.

This is likely the cause of the line width mean shifts visible in the scatter plots. For example, in Figure 4-11, the two clusters of line width were captured at opposite ends of the print, where the difference between the line widths was noticeable. There is also the factor of printing pressure. As shown in Figure 2-5, excessive print force can cause bulging of the stamp features. Since the print force often had a gradient from one end to the other, this could correspondingly bulge the features more where there is more pressure, making the lines progressively wider.

### 5.3 Long Term Inking

The multiple revolution inking tests served to validate the ‘continuous’ part of the continuous inking system. These tests showed the effects of ink retention on the stamp without replenishment from re-inking. Even though the stamp does retain enough ink after one print to continue printing more lines, those lines have notably more defects. As indicated in Figure 4-33, the quality of the prints degraded significantly after the inking stopped. Both the defect percentage and the standard deviation doubled at the end of the print compared to the beginning. The earlier printing depleted enough ink from the features that the surface coating is no longer uniform enough for additional
printing at the same quality. This validates that continuous ink replenishment is indeed required to print at these web speeds and retain high quality.

Since ink is obviously retained on the stamp after a single print, it was also desirable to determine if it was possible to have too much ink on the stamp due to continuous inkning. The little difference in quality between Samples C1 and C2 suggests that the ten revolutions of extra inking performed before contact with the substrate in Sample C2 did not affect that quality. As designed, the immersion of the stamp in the bath every revolution equilibrates the ink absorption on the surface such that there is no significant ink build up. Without ink build up, there is no reason for the print quality to degrade over time as long as the stamp remains inked enough.

5.4 Future Work

While the inking system has been shown to work, there are still some unanswered questions. It would be helpful to understand how much ink is consumed in the inking system. Qualitative observations of how quickly the ink level decreases suggest that the ink is consumed from the tank at a very high rate compared to how much is printed, for the 3ml of ink in the tank can be reduced to barely forming a meniscus with the stamp in approximately 5 printing revolutions. The liquid ink that ends up on the stamp is being evaporated by the drying system as designed. However, is it not known if only the ethanol is being lost from this, or if some HDT is being removed as well. Understanding how much ink is being consumed and comparing that to the amount of HDT being printed would shine light on the efficiency of the system.

From a design perspective, there are some modifications to the current inking system that could improve its performance and robustness in future applications. At the higher (>1in/s) web speeds, the amount of ink that flows along the stamp between the tank and the dryer is notable. High drying flows were necessary to evaporate this liquid before the print zone. However, if the bulk of this liquid could be wiped off physically with something like a doctor blade before the dryer, the dryer would have a significantly reduced load. This ink could even be recycled back into the tank.

Furthermore, at such high drying flows, the dryer has the potential to disturb the
ink in the tank purely because of the high volume of air circulating nearby. This can cause it to overflow and splatter onto the machine and the substrate. Some sort of shield to deflect to drying flow from the tank without interfering with the actual drying would alleviate this (maybe this could be combined with the ink wiper). Additionally, stamp cleanliness, especially for machines similarly not in a clean room, could create more print quality issues. Having some sort of ethanol wash before the ink is applied may help reject dirt and other contaminants.

Since this work focused on continuous inking, there were multiple printing parameters that were not significantly varied. As a result, it is unclear whether the inking system will function in a broader range of these parameters. Specifically, the print force and stamp geometry effects could cause concern. Since the print force control was open loop and not all of the print was viable from a print pressure perspective, the inking system was not required to ink and dry effectively over a large stamp area. While the tank and dryer concept should extend well to wider regions, this would be important to confirm. In regards to stamp geometry, the only features the inking system had to encounter were lines. Since these were circumferential lines on the stamp, they were aligned with the flow directions of both the liquid in the tank and the drying flow. A stamp with more complex geometry, such as transverse lines, dots and circuits, could pose issues if they interfere with the fluid dynamics of inking and drying.

In the theme of both inking efficiency and unchanged printing parameters, it would be prudent to vary the ink’s HDT concentration. The 15mM concentration was picked because it had been shown to be effective in other work, as well as initial testing. However, lower concentrations could potentially be used to conserve HDT, which is rather expensive. High concentrations of ink generally bond with the substrate faster, so increasing the concentration could be valuable to push the contact time limitations in higher speed printing.
Chapter 6

Conclusion

6.1 Thesis Contributions

This thesis work set out implement continuous inking in the context of roll-to-roll microcontact printing. To that end, literature review and empirical testing were performed to select an appropriate material system - HDT and gold. Initial trials were completed to select the ink tank concept. A complete inking and drying system was designed, implemented, and tested to confirm basic functionality. Experimentation was performed to affirm pattern consistency and measure the print quality over a range of printing parameters. Most importantly, it was established that the system performed satisfactorily at high web speeds and in a long term setting. With this, the inking system validated the continuous roll-to-roll microcontact printing process.

6.2 Next Steps

While this continuous inking system has been proven functional, there are still many challenges remaining to prove complete scalability of roll-to-roll microcontact printing. An important step forward, one that is currently in progress, is the measurement of the applied print force [38]. This will close the loop on the printing pressure, allowing much more precise management of the contact region. In addition, the measurement of the printed product must be shifted from after printing to during printing. While the current method of etching for visualization allows retrospective
analysis of quality, it does not allow for in process control. One such method, which relies on the surface energy differences between the HDT and gold to create differential regions of condensation visible to an in-line camera, is already in progress [30]. Lastly, it is crucial to experiment with a variety of printing patterns besides the current circumferential lines. A much wider range of features is necessary to create products in the desired applications. Hence, it is important to ensure the inking and control systems can handle a diverse feature set.
Appendix A

ODPA on Aluminum

In addition to the core work with HDT performed in this thesis, auxiliary experimentation with microcontact printing was performed. Printing of octadecylphosphonic acid (ODPA) on aluminum substrates was pursued in an attempt to widen the range of material systems in use.

A.1 Material System Selection

The investigation of the ODPA and aluminum material system was motivated largely by cost. Not only is aluminum significantly less valuable than gold, but ODPA is also noticeably less expensive than HDT. During this experimentation, targets for the sputter of gold and aluminum were purchased for 99$/g and 0.52$/g, respectively, while HDT and ODPA reagents cost 460$/g and 88$/g, respectively. One main advantage of high throughput manufacturing is decreased cost, so developing a lower cost material system made sense. Since OPDA was supposedly compatible with both aluminum oxide and iron substrates, it could also be valuable for the CNT patterning work discussed later.

The work of Goetting, et. al was instrumental in selecting ODPA instead of another aluminum-compatible SAM [39]. In this work, OPDA was successfully printed on the native oxide of aluminum and etched, though on a rigid substrate. This laid out the procedures necessary to perform similar printing on flexible aluminum-coated PET substrate with etching for visualization.
A.2 Initial Testing

Initial testing of the material system was performed by manually printing onto aluminum-coated PET substrate, with a very similar procedure to that described in Chapter 5. The ink was prepared to a concentration of 10mM OPDA in isopropanol. This ink was swabbed onto the surface of the stamp, dried, and then printed for 10s. The sample was then etched in Aluminum Etchant Type A for 1min and rinsed in a water bath. One such print is shown in Figure A-1, indicating a successful print. Due to the low quality substrate, there are notable pinhole defects and background contrast variation.

![Figure A-1: Initial manual plate-to-plate print of ODPA on aluminum-coated PET substrate. Print was swab-inked, dried, and brought into contact for 10s. Wet chemical etch was performed for 1min for visualization. Pattern replication is good and the lines are crisp, though the substrate has many hole defects.](image)

However, replicating the quality of these prints during roll-to-roll print proved difficult. Figure A-2 shows one of the best roll-to-roll prints created on the machine. This was swab-inked, dried, and printed at 6N print force and 0.1in/s web speed. Again, the pattern replication is good, the lines are crisp, and there are obvious substrate defects. However, other prints with the same settings, as well as other areas of this print, were simply not as high quality. Figures A-3 and A-4 give good
indications of the core issues. Instead of crisp lines, the lines are not completely filled in and have ill-formed edges. Attempts to diagnose the issue by increasing print force, changing the tool, and cleaning the substrate all proved ineffective. It was finally determined that the most likely cause was the contact time difference between the manual printing and roll-to-roll printing methods. Since the machine prints only had 1-2s of contact time compared to the 10s of the manual print, there could have not been enough time for complete ink transfer and SAM formation.

Figure A-2: Successful roll-to-roll print of ODPA on aluminum-coated PET substrate. Line quality is good. This was swab-inked, dried, and printed at 6N print force and 0.1in/s web speed with a 1min etch for visualization.
Figure A-3: Roll-to-roll print of ODPA on aluminum-coated PET substrate with fuzzy lines. Throughout the lines, SAM coverage is incomplete. This was swab-inked, dried, and printed at 6N print force and 0.1in/s web speed with a 1min etch for visualization.

Figure A-4: Roll-to-roll print of ODPA on aluminum-coated PET substrate with severe printing problems. The center area of the line seems to be missing, and the rest of the line is blotchy and partially covered. This was swab-inked, dried, and printed at 6N print force and 0.1in/s web speed with a 1min etch for visualization.


A.3 Contact Time Experiments

Consequently, more rigorous experimentation with regard to contact time was performed. The substrate used in this was a glass microscope slide coated in 100nm of aluminum\textsuperscript{1}. These were manually printed using a 100g weight with contact times ranging from 30s to 5min. The same 10mM ODPA ink was used with the swab inking strategy. All samples were etched for 2min in Aluminum Etchant Type A for visualization. Figure A-5 shows one image from each of the four samples.

It is apparent from Figure A-5 that low contact times have significantly worse prints than high contact times. The 5min contact time sample looks very good, as the lines are completely filled in and have well-defined edges. Contrastingly, the 1min and 30s contact time samples have incomplete lines and ragged edges. The lower contact times mean there is insufficient time to form a complete monolayer on the surface of the substrate, so the printed lines are imperfect.

A.4 Conclusion

Based on the results of the roll-to-roll printing and the contact time experimentation, it was clear that relatively high contact times were necessary for ODPA prints to be of acceptable quality. In light of Goetting’s work, where 10min contact time was used, this agrees well. While the ODPA and aluminum material system may be viable for plate-to-plate printing where long contact times can be used, it does not work well for roll-to-roll printing, where the contact times can easily be below 1s. Hence, further work on this material system was suspended.

\textsuperscript{1}These slides were procured from Deposition Research Laboratory, Inc. 530 Little Hills Industrial Blvd. St. Charles, MO, 63301
Figure A-5: ODPA printing contact time comparison: The prints were swab-inked with 10mM, printed for the indicated time, and wet etched for 2min. It is clear that the quality of the print degrades with decreased contact time. Sample (a) has good pattern replications and clean lines, while (c) and (d) have incomplete patterns and ragged edges.
Appendix B

CNT Catalyst Patterning

B.1 Goals

As mentioned in Chapter 1, carbon nanotubes (CNTs) can have useful applications as battery electrodes. However this application requires that the CNT forests be grown in specific patterns. Currently, this is done with standard lithography practices on rigid silicon substrates. If microcontact printing could be used to pattern the CNT growth catalyst, it could enable a less expensive patterning method, especially if it could be used in a roll-to-roll context.

The CNT catalyst used in this work is made on a rigid silicon substrate which has 1nm of iron deposited on top of 10nm of aluminum oxide (alumina). Both elements need to be present for CNT forest growth to occur. Hence, patterned forests can be created by removing the iron from the alumina, removing both catalyst elements, or adding iron to a base layer of alumina.

This work was performed in collaboration with Bethany Lettiere, a student in the Mechanosynthesis lab. She was responsible for preparation of the samples and the CNT growth processes.

B.2 Strategy 1: Printing and Etching with ODPA

The first strategy that was tried to pattern the catalyst was to print ODPA directly onto the catalyst. Literature had indicated that ODPA would form monolayers on the
iron surface [40]. The ODPA would be used as an etch resist to remove the catalyst in the unprinted areas, so the forests would grow in the printed pattern, as shown in Figure B-1.

**Figure B-1:** Schematic diagram CNT catalyst patterning using microcontact printing of ODPA. The ODPA serves as an etch resist, so wet chemical etching removes the catalyst in the unprinted areas, and the CNT forests are grown in the printed pattern.

Initial testing of this was performed with manual printing on the rigid substrate. The 5mM ODPA in isopropanol was inked onto the stamp with a swab, dried, and printed for 10s. These samples were then etched in a bath of 1:1 mixture of HCl and deionized water for 10s and then rinsed with water. Thereafter, CNT growth with 10min anneal and 20min growth phase was performed. Figure B-2 shows some of the success achieved with this method. On the right side, there are CNT forests that have grown in the region where the ODPA was printed. It is clear, however, that much of the printed lines have not had any CNT growth, and that CNT growth has occurred in areas outside of the printed lines. This result was encouraging because it showed that the method could work, but more investigation was necessary to ensure it would work consistently.

Since the catalyst was deposited on a rigid substrate, printed was limited to manual plate-to-plate printing or roll-to-plate printing with the Petrzelka machine. Efforts to create uniform prints with the roll-to-plate machine were unsuccessful. Calibration of the force and moment controller was finicky, and the roll would not balance evenly during printing of the small wafer samples. Hence, the print pressure was very non-uniform, and the prints were inadequate. Further printing was limited to manual printing, which also means there is difficult controlling contact force reliably. A trained hand, however, meant that such prints were generally not complete failures. With the manual printing, replicating the initial CNT growth proved very difficult.
As shown in Figure B-3, the ODPA lines were blotchy and inconsistent. Around the time of this work, the contact time issue referred to in Appendix A was confirmed, meaning high contact times were necessary to get good ODPA prints. Hence, it was determined that this processing method was not worth pursuing further.

Figure B-2: Scanning electron micrograph of patterned CNT forest growth. On the right side, there are CNT forests that have grown in the region where the ODPA was printed. On the left, however, much of the printed lines have not had any CNT growth and CNT growth has occurred in areas outside of the printed lines. The sample was manually printed with 5mM ODPA for 10s It was etched in a bath of 1:1 mixture of HCl and deionized water for 10s and then rinsed with water. Thereafter, a CNT growth with 10min anneal and 20min growth phase was performed.
B.3 Strategy 2: Printing Iron Nanoparticles

Further literature review revealed a strategy of microcontact printing CNT catalyst directly onto the substrate [41]. In the work of Kind et al, iron nanoparticle ink was printed on silicon substrate, and then grown into CNTs. An attempt to replicate this work was made by printing this same ink onto the alumina-coated silicon substrate currently used as part of the CNT catalyst.

The ink was created by mixing ferric nitrate nonahydrate into ethanol to create a 100mM solution of $Fe^{3+}$. This was swabbed onto the surface of the stamp, dried, and printed with at least 10s for each step. Figure B-4 shows one such print, clearly indicating non-uniform transfer. The ink seemed to coalesce into droplets in the areas it should be patterned. When prints such as this were put through the growth process, CNTs only formed in the locations of these droplets, indicating those were the only regions with high enough iron concentration to grow effectively.

**Figure B-3:** Reflection micrograph of ODPA manually printed on CNT catalyst. The ODPA lines are highly inconsistent in width and display ill-formed edges.
In an attempt to make the printed layer more uniform, the PDMS stamp was plasma treated to increase its surface energy. The stamp was put in the plasma oven (Technics Plasma Exciter 300-1) for 5min of vacuum time and 2min of plasma exposure. Contact angle measurement of water on the stamp indicated this reduced the contact angle from around 65° to 20°. While the wetting of the ink on the surface of the stamp was significantly improved, additional printing and growth showed no clear improvement in the uniformity of the CNTs. Without any real success or a good understanding of the transfer mechanics, this strategy was abandoned.

![Image of iron nanoparticle ink onto aluminum oxide](image)

**Figure B-4:** Print of iron nanoparticle ink onto aluminum oxide. The intended line print is barely visible, as the ink has coalesced into large droplets instead of creating a uniform printed layer.

### B.4 Strategy 3: Gold Poisoning with HDT

Another strategy tried was to ‘poison’ the growth of the CNTs with gold. In this setup, gold is deposited on top of the usual catalyst iron/alumina catalyst. The gold would inhibit the gases from reacting with the iron inside the furnace, effectively inhibiting CNT growth. Using the proven HDT/gold material system would ensure
good patterning. This would create an inverse pattern of CNTs, as etching of the sample would leave gold inhibitor lines, and the CNTs would grow in between.

To test this concept, the individual steps were validated separately. First, it was confirmed that depositing a 1nm layer of gold on the usual 1nm iron and 10nm alumina catalyst did indeed inhibit growth. Next, gold-coated catalyst wafers were etched with the thiourea/ferric nitrate etchant for the usual 2min to remove the gold. X-ray Photon Spectroscopy (XPS) confirmed the gold was indeed removed from the catalyst. These etched wafers had successful CNT growth, indicating the etching process did not damage the catalyst underneath the gold.

The complete printing, etching, and growth steps were then combined. 15mM HDT was swab-inked onto a stamp, dried, and manually brought into contact with the substrate for 10s. The samples were then etched for 2min to remove the gold. When CNT growth was performed with these samples, however, no growth was apparent. This was rather confusing, as the individual steps had all been shown to function as expected. Currently, it is suspected that the gold diffuses across the surface of the substrate at the high temperatures during the growth process, effectively forming an inhibitor layer over the substrate. Further work is required to confirm this theory.
Appendix C

Image Processing Code

C.1 Pre-Processor

```
function [ImOut] = ImProcess1(Im)

%% ImProcess1 performs basic pre-processing on line images

% Im in the input image file (uint8)
% Convert to grayscale
ImG = rgb2gray(Im);

% figure
warning off
imshow(ImG)
figure
% warning off

%% Invert image
ImGI = imcomplement(ImG);

%% Background Creation
ImBackground = imopen(ImGI,strel('disk',60,4));

% Values are currently arbitrary and need to be double checked. ...
% I'm not

% sure I'm using the strel command correctly
% figure
% warning off
```
% imshow(ImBackground)

%% Background Subtraction
ImGI2 = ImGI - ImBackground;

%% Crop Image
% To deal with non-uniform lighting, cutting off edges
Dim = size(ImGI2);
HCrop = round(Dim(2) * [.1 .9]); % Horizontal crop points
VCrop = round(Dim(1) * [.1 .9]); % Vertical crop points

ImGI2C = ...
    imcrop(ImGI2,[HCrop(1),VCrop(1),HCrop(2)-HCrop(1),VCrop(2)-VCrop(1)]);

%% Contrast adjust
ImGI3 = imadjust(ImGI2C);

%% Thresholding
thresh = graythresh(ImGI3);

%% Create BW Image
ImBW = im2bw(ImGI3,thresh);
% Image is color inverted from original

%% Create edge detection image for Hough Transform
% Performs edge detection and rotates image to vertical
ImERot = imrotate(edge(ImGI3,'Sobel',0.05,'horizontal'),90);
% Hough transform to find image orientation and horizontally align
AngleRes = 0.1; % Resolution of Hough Transform
AngleLimit = 2;
AngleRange = -AngleLimit:AngleRes:AngleLimit-AngleRes; % Array of ...
    [H,T,R] = hough(ImERot,'Theta',AngleRange);

% figure
% imshow(imadjust(mat2gray(H)),'XData',T,'YData',R,...
% 'InitialMagnification','fit');
% xlabel('\theta'), ylabel('\rho');
% axis on, axis normal;
% colormap(hot)

peaks = houghpeaks(H,5);

% figure
P = peaks;
% imshow(H,[],'XData',T,'YData',R,'InitialMagnification','fit');
% xlabel('	heta'), ylabel('ho');
% axis on, axis normal, hold on;
% plot(T(P(:,2)),R(P(:,1)),'s','color','white');

lines = houghlines(ImERot,T,R,peaks,'FillGap',5,'MinLength',7);

% figure, imshow(ImERot), hold on
% for k = 1:length(lines)
% xy = [lines(k).point1; lines(k).point2];
% plot(xy(:,1),xy(:,2),'LineWidth',2,'Color','green');
% % Plot beginnings and ends of lines
% plot(xy(1,1),xy(1,2),'x','LineWidth',2,'Color','yellow');
% plot(xy(2,1),xy(2,2),'x','LineWidth',2,'Color','red');
% end

angle = mean(AngleRange(peaks(:,2)));
% Looks right, should triple check
ImOut = imrotate(ImBW,angle,'Crop');

end

C.2 Main Processor

function [WidthsOut,DefectsOut] = ...
   ImProcess3(ImBW,Scale,LineWidth,LinePitch)
%% ImProcess3 performs line width analysis on pre-processed images

% Attempting to add defect detection over ImProcess2

% ImBW in the input image file from ImProcess1 (logical)
% Scale is the image scale in micron/pixel
% LineWidth is the expected line width in microns
% LinePitch is the period of the print in microns

% WidthsOut is a list of line width [Mean Std]
% DefectsOut is a list of percentage of line which is defective

%% Get image dimensions
Dim = size(ImBW);

%% Average picture along edge
Mean1 = mean(ImBW,2);

%% Peak Detection
MinSep = (LinePitch-LineWidth)/Scale; % Expected line separation ...
in pixels
MinSep = MinSep*0.8; % Fudge factor to give some margin on line ...
separation

[Peak1,Loc1] = ...
    findpeaks(Mean1,'MinPeakHeight',.5,'MinPeakDistance',MinSep);
% Height of .5 is pretty reasonable
% Distance is based on resolution and expected print parameters

%% Basic width measurement
N = length(Peak1); % Number of peaks detected => Number of lines
WidthRange = ceil((LineWidth/Scale)*1.4); % Number of pixels ...
    around peak that will be checked for line
% Fudge factor of 40% to detect everything

% WidthRange must be even
if mod(WidthRange,2) ≠ 0
    WidthRange = WidthRange + 1;
HeightThresh = 0.1; % Min height to be included in measurement
% Do I even need this on a black and white image?

%% Find centerlines
[Widths1,Centers1] = deal(zeros(N,1));

for i = 1:N
    Region = Loc1(i) + [-WidthRange/2:WidthRange/2]; % Region of pixels to check
    Region(Region ≤ 0) = []; % Remove region out of picture
    Region(Region > Dim(1)) = [];
    ValidRegion = Region(Mean1(Region)＞HeightThresh); % Pulls all values in region above height threshold
    Widths1(i) = length(ValidRegion); % Calculates valid region width
    Centers1(i) = ValidRegion(round(length(ValidRegion)/2)); % Midpoint of valid region
end

%% Pre-allocate
[Widths2,Defects] = deal(zeros(N,Dim(2)));
[WidthsOut,NonDefectRange] = deal(zeros(N,2));
[DefectsOut, NormalCheck] = deal(zeros(N,1));

% Number of standard deviations from the mean a width must be to count as a defect
DefectThresh = 1; % ARBITRARY

% Percentage from mean a width must be to count as a defect
DefectPercent = .2;

for k = 1:N; % For each centerline
    Region2 = Centers1(k) + [-WidthRange/2:WidthRange/2]; % Region to check around the centerline
Region2(Region2 &lt;= 0) = []; %Remove region that is out of picture
Region2(Region2 &gt; Dim(1)) = [];

for j = 1:Dim(2); %Along each column
    Widths2(k,j) = sum(ImBW(Region2,j))*Scale; %Sum along ... line and Convert to microns
    % Defects2(k,j) = std(ImBW(Region2,j))*Scale;
end

% Plot along line
% figure
% plot(Widths2(k,:))

%% Create stats
WidthsOut(k,1) = mean(Widths2(k,:)); %Mean
WidthsOut(k,2) = std(Widths2(k,:)); %Std Dev
NormalCheck(k) = ...
    ztest(Widths2(k,:),WidthsOut(k,1),WidthsOut(k,2)); %Is the ... data normally distributed

%% Calculate Defects
% Range of line widths for line that defines not defective
% NonDefectRange(k,:) = ...
[WidthsOut(k,1)-DefectThresh*WidthsOut(k,2) ...
    WidthsOut(k,1)+DefectThresh*WidthsOut(k,2)];

NonDefectRange(k,:) = [1-DefectPercent ... 
    1+DefectPercent].*WidthsOut(k,1);

% Calculate defective pixels
Defects(k,:) = (Widths2(k,:)&lt;NonDefectRange(k,1)) + ... 
    (Widths2(k,:)&gt;NonDefectRange(k,2));
DefectsOut(k) = sum(Defects(k,:))/Dim(2) * 100; %Sum defects. ...
    Convert to percentage
end
end
Bibliography


